

The Limits of Low-Temperature Performance of Li-Ion Cells

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The results of electrode and electrolyte studies reveal that the poor low-temperature (<−30°C) performance of Li-ion cells is mainly caused by the carbon electrodes and not the organic electrolytes and solid electrolyte interphase, as previously suggested. It is suggested that the main causes for the poor performance in the carbon electrodes are (i) the low value and concentration dependence of the Li diffusivity and (ii) limited Li capacity.

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Li-ion batteries are widely used at room temperature because of their high specific energy and energy density, long cycle life, low self-discharge, and long shelf life.¹⁻³ For certain defense and space applications they are required to be used at low temperatures (<−30°C). In general they exhibit poor low-temperature performance. For example, it has been reported that the capacity of Li-ion cells at −40°C is 12% of the room temperature value.⁴ It has been suggested that the poor performance of Li-ion batteries at low temperatures is due to the electrolyte, which determines Li-ion mobility between the electrodes and the transport properties of the passivation film on the carbon anode.⁴⁻⁸ Most previous studies have focused on the development of low-temperature electrolytes. However, recent preliminary studies by Huang *et al.* suggest that the primary cause of the poor Li-ion cell performance at low temperature is related to Li-ion diffusion in the carbon anode and not in the electrolyte or passivating film.⁹

It is the purpose of this paper to confirm that the poor Li-ion cell performance at low temperature (<−30°C) is controlled by slow Li-ion diffusion in the carbon anode and not in the electrolyte or in the passivating film on the carbon anode by evaluating the following at low temperature: (i) electrolytes, (ii) cathode performance, (iii) solid electrolyte interphase (SEI), (iv) anode performance, and (v) effect of the electrode active material particle size.

Experimental

Electrolyte.—The electrolytes evaluated in this study were chosen because of previous low-temperature Li-ion battery studies of the Jet Propulsion Laboratory (JPL).¹⁰ Four carbonate-based solvent electrolytes were tested: (i) 1.0 M LiPF₆ ethylene carbonate (EC):diethyl carbonate (DEC):dimethyl carbonate (DMC) (1:1:1 vol %); (ii) 0.9 M LiPF₆ EC:DEC:DMC:propylene carbonate (PC) (3:3:3:1); (iii) 0.8 M LiPF₆ EC:DEC:DMC:ethyl methyl carbonate (EMC) (3:5:4:1), and (iv) 0.8 M LiPF₆ EC:DEC:DMC:EMC (3:5:4:2). The electrolytes, purchased from Mitsubishi Chemical Company, were sealed in glass tubes in a glove box. The samples were put into a low-temperature chamber, and the temperature was lowered first to −20, then to −30, −35, −40, and finally to −42.5°C. The samples were kept at each temperature for 4 days. The electrolyte liquidus range at low temperatures was evaluated through visual inspection. In the case of 1.0 M LiPF₆ EC:DEC:DMC (1:1:1), the solid phase that formed at −35°C was separated and analyzed using a gas chromatograph coupled with a mass spectrometer.

Electrode.—The electrode materials investigated were: mesocarbon microbead (MCMB) graphite, coke, and LiCo_{0.2}Ni_{0.8}O₂. MCMB graphite and coke were chosen because of their potential as anodes in Li-ion batteries as a result of their high specific capacity and long cycle life. LiCo_{0.2}Ni_{0.8}O₂ was investigated because of its potential as

a cathode in Li-ion batteries as a result of its relatively high specific capacity and more importantly, its high Li diffusion coefficient.

To evaluate the low-temperature performance of MCMB graphite, coke, and LiCo_{0.2}Ni_{0.8}O₂, half-cells were used. A spiral-wound configuration was used for the half-cells. The half-cells consisted of Li foil (76.2 μm, Cypress Foote) pressed onto high-purity nickel mesh substrates, a Celgard 2500 separator, a 0.8 M LiPF₆ EC:DEC:DMC:EMC (3:5:4:1) (Mitsubishi Chemical Co.) electrolyte (see the next section for the reason for this electrolyte choice), and the working electrode. The working electrodes were made by spraying a slurry onto high-purity aluminum or copper foil substrates. For the case of LiCo_{0.2}Ni_{0.8}O₂, the slurry consisted of 89 wt % LiCo_{0.2}Ni_{0.8}O₂ powder, 6 wt % Shawanigan black, 5 wt % polyvinylidene difluoride (Aldrich), all in cyclopentanone (Fluka). These electrodes typically had dimensions of 179 mm × 38.1 mm × 254 μm and a loading of 47.7 mg/cm². The carbon electrodes were made in a similar fashion; MCMB 1028 (10 μm diam, heat-treated at 2800°C) graphite, and 6 or 25 μm diam coke particle powders were used as the active material. The carbon electrodes were typically 254 μm thick with a loading of 26.7 mg/cm². The electrode processing and cell assembly were conducted in a dry room (<0.5% humidity). The half-cells were filled with electrolyte in an argon-filled glove box and then sealed in a stainless steel can. Cell performance was evaluated using galvanostatic methods. Low-temperature electrochemical studies were conducted by allowing the half-cells to remain at the desired temperature in a low-temperature chamber for 4 days before cycling.

Results and Discussion

To determine which Li-ion cell components limit low-temperature performance (<−30°C), each component (electrolyte, LiCo_{0.2}Ni_{0.8}O₂, MCMB graphite, and MCMB coke) was tested individually.

Electrolyte.—Since a Li-ion cell containing liquid electrolyte cannot be cycled if the electrolyte is frozen, the electrolyte was tested first. The test results are shown in Table I. From Table I it is observed that the 0.8 M LiPF₆ EC:DEC:DMC:EMC (3:5:4:1) electrolyte is the only one that was completely liquid at −40°C and below. In the other three electrolytes at −40°C, a solid phase was observed at the bottom of the test vials. Gas chromatograph analysis revealed that for the 1.0 M LiPF₆ EC:DEC:DMC (1:1:1) electrolyte the solid phase that formed at −35°C was EC. In summary, of the four electrolytes tested, 0.8 M LiPF₆ EC:DEC:DMC:EMC (3:5:4:1) was the one most suitable for low-temperature electrochemical evaluation of MCMB graphite, coke, and LiCo_{0.2}Ni_{0.8}O₂.

LiCo_{0.2}Ni_{0.8}O₂.—A LiCo_{0.2}Ni_{0.8}O₂ half-cell was given one cycle at room temperature using 0.22 and 0.44 mA/cm² charge and discharge current densities, respectively (Fig. 1). These current densities correspond to C/10 and C/5 charge and discharge rate used for the JPL Li-ion batteries for space applications at room temperature. Next, the half-cell temperature was lowered to −30°C for 4 days before

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Table I. Electrolyte phases at low temperature.

Label	Composition	-30°C	-35°C	-40°C	-42.5°C
1	EC:DEC:DMC (1:1:1)/1.0 M LiPF ₆	Liquid 100%	Liquid and solid coexist	Liquid and solid coexist	Solid 100%
2	EC:DEC:DMC:PC (3:3:3:1)/0.9 M LiPF ₆	Liquid 100%	Liquid and solid coexist	Solid 100%	Solid 100%
3	EC:DEC:DMC:EMC (3:5:4:1)/0.8 M LiPF ₆	Liquid 100%	Liquid 100%	Liquid 100%	Liquid 100%
4	EC:DEC:DMC:EMC (3:5:4:2)/0.8 M LiPF ₆	Liquid 100%	Liquid 100%	Liquid and solid coexist	Liquid and solid coexist

cycling at the same rates. It was observed that the half-cells could not be charged (Li deintercalated) at the same current densities as those used at room temperature (Fig. 2a). A large overpotential was observed, possibly associated with phase nucleation at the beginning of charging at -30°C. This overpotential was so large that the upper bound cutoff voltage (4.3 V) was reached immediately, thus preventing the half-cell from charging. To remedy this, a relatively low current density (0.07 mA/cm²) was used at the beginning of charging. Once the two-phase equilibrium plateau was reached (typically at 3.9 V), a current density of 0.22 mA/cm² was applied (Fig. 2b). Adding the low-current-density step at the beginning of charging enabled the cathode half-cells to be cycled at -30°C. Approximately

60% of the room-temperature capacity was retained at -30°C. This corresponds to a capacity of about 110 mAh/g at -30°C using a room-temperature capacity of 180 mAh/g for LiCo_{0.2}Ni_{0.8}O₂.¹¹ This value is about equal to that for the room-temperature capacity of the LiMn₂O₄ (ca. 120 mAh/g) cathode material.¹¹ Consequently, LiCo_{0.2}Ni_{0.8}O₂ can be used as a cathode at -30°C.

Graphite and coke.—Up to this point both the LiCo_{0.2}Ni_{0.8}O₂ cathode material and electrolyte selected are suitable for operation in Li-ion batteries at low temperatures. Next, the potential anode materials, MCMB graphite and coke were evaluated. Before cycling at low temperatures, the graphite and coke half-cells were cycled at room temperature for five cycles (at 0.285 mA/cm²) to assure complete passivation (SEI formation) and were left in the fully discharged state. Once the half-cells were at -40°C, they were charged (Li extracted, Fig. 3 and 4). From Fig. 3 and 4, approximately 87% of the room-temperature capacity was retained for graphite and 86% for coke. However, when attempting to discharge both the graphite and coke half-cells, the lower bound cutoff potential (0 V vs. Li/Li⁺) was reached immediately with about 0% discharge capacity. From this it is apparent that at -40°C at a current density of 0.285 mA/cm², Li can be extracted from graphite and coke but cannot be inserted under the same conditions.

If the SEI acts to control low-temperature behavior, no difference would be expected in behavior for the case of Li insertion and extraction for both coke and graphite. For example, it is unlikely that the SEI can act as a diode and impede Li insertion and not extraction. The results shown here at -40°C reveal that the SEI does not limit low-temperature performance. This is in contrast to previous investigations which suggest that the SEI limited cell performance at low temperature.⁸

Based on these results we suggest that the poor low-temperature performance for Li-ion cells is related to Li-ion diffusivity in carbon (graphite and coke). This is proved in the following paragraphs.

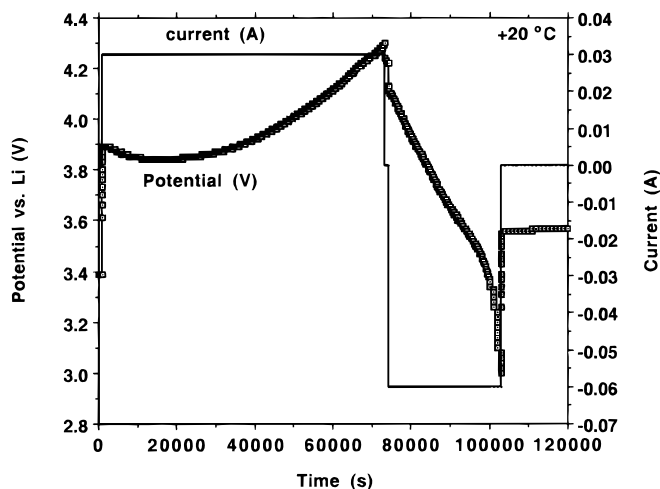


Figure 1. The Li/LiCo_{0.2}Ni_{0.8}O₂ half-cell was cycled for one cycle at room temperature using 0.22 and 0.44 mA/cm² charge and discharge current densities, respectively. The electrode area is 136.4 cm².

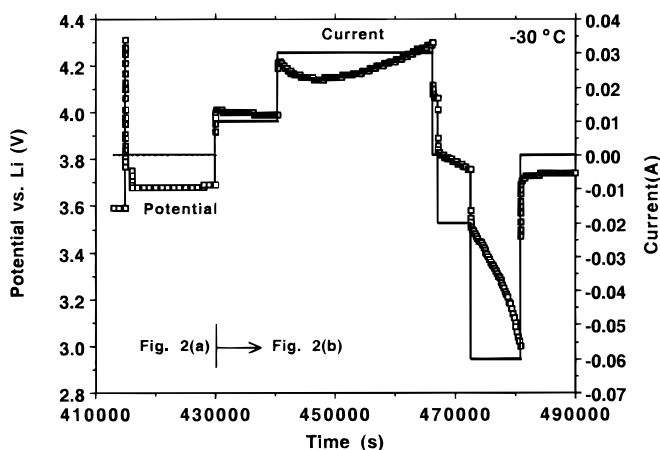


Figure 2. (a) At -30°C, the half-cells could not be charged at the same current densities as those used at room temperature. (b) The addition of the low current steps at the beginning of charging and discharging enabled the cells to be cycled. The electrode area is 136.4 cm².

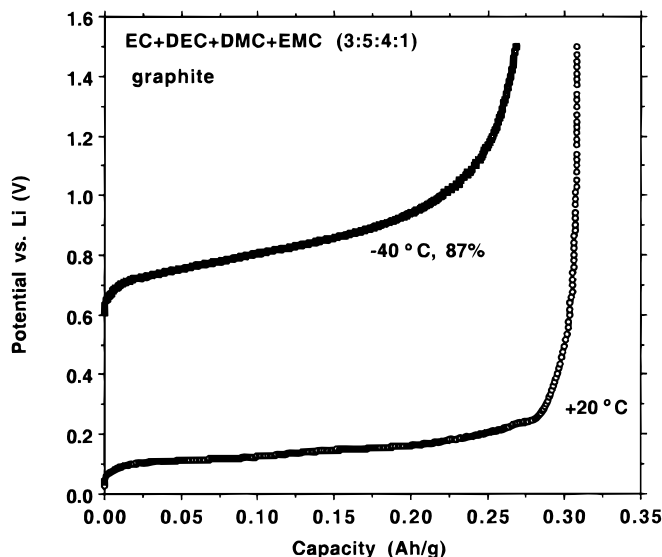


Figure 3. The Li/graphite half-cell was charged (Li extracted) at -40°C after discharging (Li intercalation) at room temperature.

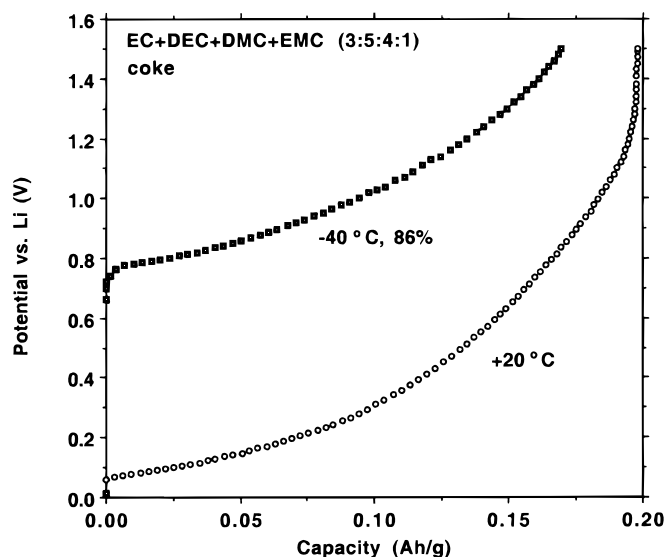


Figure 4. The Li/coke half-cell was charged (Li extracted) at -40°C after discharging (Li insertion) at room temperature.

It has been shown that Li can be extracted from graphite and coke at -40°C using 0.285 mA/cm^2 . Since the same current densities could not be used to insert Li into coke or graphite, a significantly lower current density was used. This was done to determine whether there is a kinetic limitation in graphite and coke that comes from the concentration-dependent polarization that occurs during Li insertion at low temperature. The discharge curves, which represent Li insertion, for graphite using current densities of 0.285 mA/cm^2 at room temperature and 0.0095 and 0.00095 mA/cm^2 at -40°C are shown in Fig. 5. From Fig. 5, the half-cell discharge capacity at room temperature was 282 mAh/g , at -40°C using 0.0095 mA/cm^2 the capacity was 12 mAh/g , and at -40°C using 0.00095 mA/cm^2 the capacity was determined to be 216 mAh/g . From this it is apparent that there is a significant decrease in capacity when comparing curves 1 and 3 in Fig. 5. This is despite the fact that the current density is 30 times less at -40°C than at room temperature. Additionally, by lowering the current density by 300 times less than the room-temperature current density, approximately 77% of the room-temperature

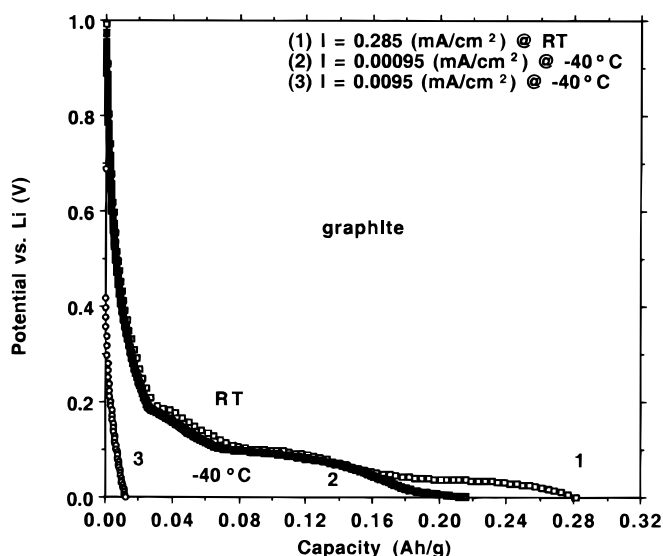


Figure 5. The discharge curves, which represent Li intercalation, for graphite using current densities of 0.285 mA/cm^2 at room temperature and 0.0095 and 0.00095 mA/cm^2 at -40°C .

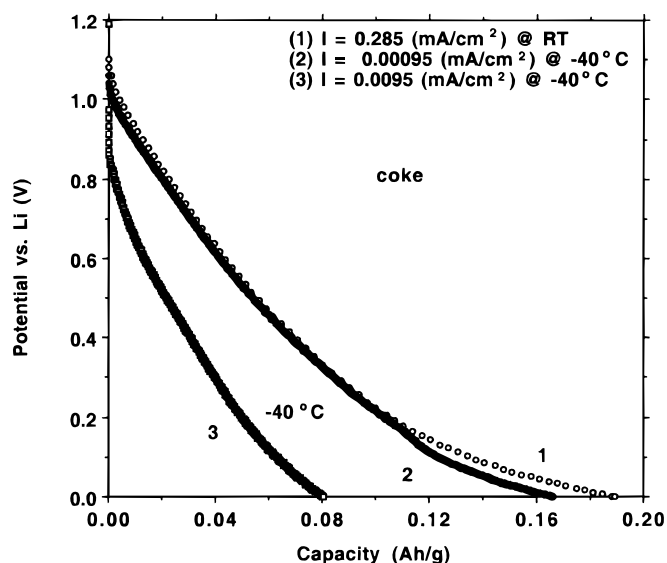


Figure 6. The discharge curves, which represent Li insertion, for coke using current densities of 0.285 mA/cm^2 at room temperature and 0.0095 and 0.00095 mA/cm^2 at -40°C .

capacity was retained at -40°C . The fact that more Li can be inserted at lower current densities at -40°C suggests that the Li insertion reaction is kinetically limited at low temperature. This is discussed in more detail in the following sections.

The same test was performed on coke half-cells (Fig. 6). In Fig. 6, the specific capacities were determined to be 189 , 166 , and 81 mAh/g for curves 1, 2, and 3, respectively. Here it is interesting to note that at 0.0095 mA/cm^2 and -40°C coke retained 43% of its room-temperature capacity. In comparison, graphite under the same conditions retained only 4% of its room-temperature capacity. Given this information, combined with the fact that both the graphite and the coke particle sizes were approximately the same, it is believed that the large low-temperature capacity in coke can be attributed to its higher Li diffusivity value compared to graphite. At room temperature, Li diffusivity in coke is $10^{-9}\text{ cm}^2/\text{s}$ vs. $10^{-11}\text{ cm}^2/\text{s}$ graphite.¹² Thus, if the same trend holds (Li diffusivity in coke > Li diffusivity in graphite) at low temperatures, it is expected at -40°C and at the same rate that the relatively slow Li diffusion in graphite would cause a significant concentration polarization to occur (Fig. 7a). Concentration polarization lowers the cell voltage and thus, the lower-bound cutoff voltage is reached far before each particle has reached its usable capacity. The same, however, does not occur during Li extraction because Li diffusivity actually increases at the surface of each particle due to its lower Li concentration (Fig. 7b). In coke, where Li diffusion is much faster than in graphite, there is a lower concentration polarization compared to graphite. Hence, the cell potential for coke, under the same conditions as graphite, does not drop as fast and thus, more of its usable capacity is retained at low temperatures before the lower-bound cutoff potential is reached.

To support further the argument that low-temperature Li-ion performance is limited by Li diffusion in carbon, the effect of particle size on the specific capacity of coke at -40°C was investigated. To accomplish this, two coke half-cells were assembled. One half-cell contained coke with $6\text{ }\mu\text{m}$ diam particles and the other $25\text{ }\mu\text{m}$ diam particles. After five cycles at room temperature, the temperature of the cells were lowered first to -20°C and cycled then to -30°C and cycled all using 0.11 mA/cm^2 on charge (Li extraction) and 0.055 mA/cm^2 on discharge (Li insertion, Fig. 8). From Fig. 8, the 6 and $25\text{ }\mu\text{m}$ coke particles had almost the same reversible capacity, about 196 mAh/g for the first two cycles at room temperature. However, when the temperature was lowered to -20°C the $25\text{ }\mu\text{m}$ diam coke particle specific capacity decreased by 64% of the room-temperature capacity, while the $6\text{ }\mu\text{m}$ diam coke particle specific capacity only decreased by 35% of the room-temperature capacity. Simi-

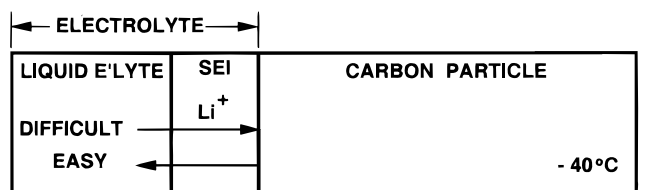


Fig. 7(a) Li intercalation

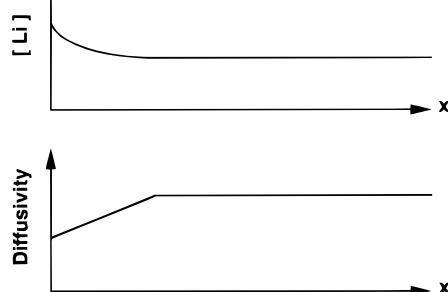
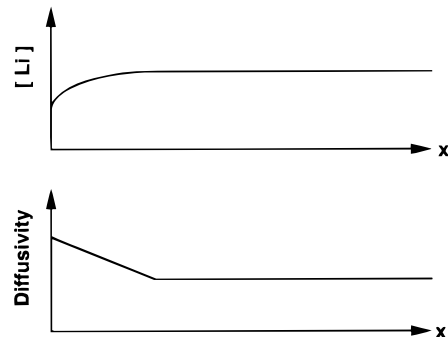


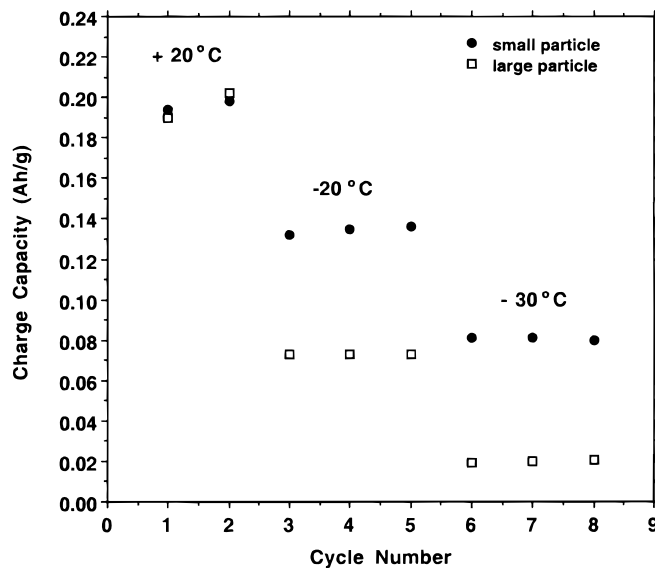
Fig. 7(b) Li de-intercalation

**Figure 7.** Schematic diagram showing the Li concentration and diffusivity profiles in graphite during Li intercalation and deintercalation at -40°C .

larly, when the temperature was lowered to -30°C , the $25\text{ }\mu\text{m}$ diam coke specific capacity decreased by 90% of the room-temperature capacity, while the $6\text{ }\mu\text{m}$ diam coke particle size specific capacity decreased by only 59% of the room-temperature capacity. Furthermore, when the temperature was lowered to -40°C , both the 6 and $25\text{ }\mu\text{m}$ diam coke materials have almost no capacity. The fact that particle size affects the capacity at low temperatures supports the contention that Li diffusivity limits low-temperature performance. In the larger particles, Li diffusion lengths are longer than in the smaller particles. This causes a higher concentration polarization to develop on the larger particle surfaces compared to the smaller particle surfaces. As a result of the lower concentration polarization at the surface of the smaller particle, the half-cell voltage remains higher compared to that for the larger particles during the discharge. If, as described earlier, the half-cell voltage stays above the cutoff voltage longer, more of its usable capacity can be retained. Thus, the smaller-particle-size coke should and does exhibit a higher capacity compared to the larger-particle-size coke at low temperature. This result adds further proof to the suggestion that the poor performance of carbon at low temperature ($<-30^{\circ}\text{C}$) is due to Li diffusion in the carbon.

Conclusions

The results of electrode and electrolyte studies reveal that the poor low-temperature ($<-30^{\circ}\text{C}$) performance of Li-ion cells, for this

**Figure 8.** Effect of the coke particle size on charge capacity at low temperatures.

system, is mainly caused by the carbon electrodes and not the organic electrolytes and SEI, as previously suggested. It is suggested that the main causes for the poor performance in the carbon electrodes are (i) the low value and concentration dependence of the Li diffusivity and (ii) limited Li capacity. Consequently, an alternative electrode material to carbon must be developed in order to improve both capacity and rate capability of Li-ion cells at low temperature ($<-30^{\circ}\text{C}$).

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